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CATALYTIC AGENT DEGRADATION ON OXIDE FILMS AND IN MICROHETEROGENEOUS SOLUTION SYSTEMS

Third Interim Report

by

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DTIC ELECTE JAN 15 1991 S E D

December 20, 1990

United States Army

European Research Office of the U.S. Army
London, England

CONTRACT NO. DAJA45-90-C-0007

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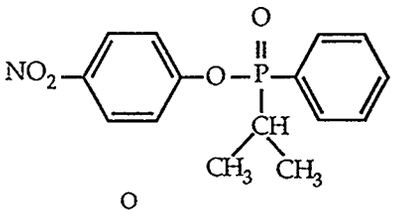
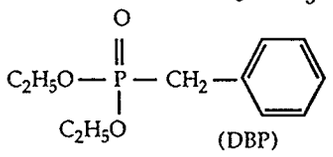
Homogeneous solutions of iron" complexes are extremely efficient catalysts in the decomposition of organophosphorous compounds. Both the effect of the oxidation state of iron and of the iron's complexing anions on the catalytic activity of these iron complexes have been investigated. To date our laboratory has documented the usage of Fe(III) oligomers as a catalyst in the degradation of several simulant organophosphorous compounds, i.e. 4-NPIPP (4-nitrophenylisopropylphenylphosphinate), DBP (diethylbenzylphosphonate), and DEP diethylethylphosphonate) according to the following equations:



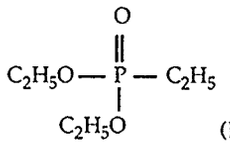
$$+ \ 19.5\ O_2 \longrightarrow 15\ CO_2 + H_3PO_4 \quad (1$$

$$+ \ HNO_3 + 6H_2O$$



(DBP)

$$+ \ 15\ O_2 \longrightarrow 11\ CO_2 + H_3PO_4 + 7\ H_2O \quad (2)$$



(DEP)

$$+ \ 9.5\ O_2 \longrightarrow 6\ CO_2 + H_3PO_4 + 6\ H_2O \quad (3)$$

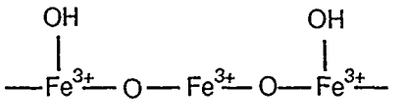
The nature of the iron salts used as precursors for the oligomers as well as the concentration of iron relative to that of the toxic compound (specifically, DBP) effect the degradative rate efficiency of these compounds. Ferric chloride complexes augmented the initial reaction rate relative to the sulfate and nitrate iron (III) complexes, but their catalytic activity diminished during the course of the reaction (see Fig. 1)

Amongst these various ferric salts $Fe(NO_3)_3$ appeared to be the most catalytically active, the initial reaction rate being vey rapid attaining the theoretical total decomposition threshold within 30 minutes. Simultaneous heating and irradiation with wavelengths longer than 435 nm enhances this decomposition dramatically, forcing even the room temperature experiments to attain theoretical degradation limits of CO_2 evolution (see Fig. 2).

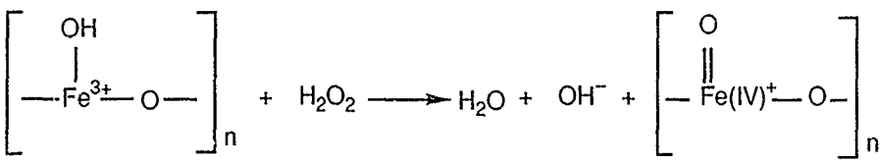
Iron to toxic compound ratios greater than 1 to 1, i.e. either 3 to 1 or 2 to 1 likewise enhance the initial reaction rates. Addition of salts such as $NaNO_3$, Na_2SO_4 and NaCl has a deleterious effect on the catalytic activity in presence of

both $Fe(NO_3)_3$ and $FeCl_3$, these anions having essentially no effect when used in conjunction with the catalyst $Fe_2(SO_4)_3$. The age of the catalytic preparation apparently has an effect on its catalytic activity, freshly prepared catalysts being much more active. This decline in activity upon ageing is most likely due to iron hydroxide formation, a form proven experimentally to be inactive catalytically in promoting these decompositions (see Fig. 3).

As mentioned previously, when discussing the role of ferric sulfate in the rapid oxidation of the organophosphate compounds, it should first be noted that the ferric ions form a 1:1 complex with sulfate (association constant $1.41 \cdot 10^4$) in aqueous solution. At neutral pH this is likely to undergo condensation reactions to yield oligomers or polymers where the individual ferric sulfate units are linked through oxygen bridges:



Thus, the Fe (III) could be present in our solutions in different forms, the catalytically active one remaining yet to be determined. The catalytic intervention of such iron (III) species could occur via two different pathways. The first involves formation of an Fe (IV) complex formed by O-transfer from hydrogen peroxide, according to the following reaction:



This is a very powerful oxidant capable of attacking the organophosphate (see Fig. 4). The second mode of decomposition involving the reduction of Fe(III) to Fe(II) by the organophosphate which would subsequently undergo a Fenton-type reaction with hydrogen peroxide generating hydroxyl radicals to be used as oxidants of the CW simulant has been disqualified through experimentation. The formation of a thermal and photoactive Fe (IV)-DBP complex is, however, depicted in Fig. 5 where the difference spectrum of a Fe(III)-DPB-H_2O_2 solution with a Fe(III)-DPB-H_2O reference is shown. Here the formation of a higher oxidative state species is ascertained by the rapid growth

of an absorbance peak with a maximum at ~400 nm. This peak decays fairly quickly at ambient temperature (continuous lines), but its room temperature degradation is accelerated by irradiation in the solar simulator (hatched lines).

There is not enough energy available at the temperatures studied to allow the formation of hydroxyl radicals by simple thermal dissociation (~1eV binding energy for H_2O_2), as is possible at elevated temperatures for persulfate.

TiO_2 plays a stabilizing role in these experiments. Thus in TiO_2 containing solutions there is very little difference in degradation efficiency between 0.02 M and 1M H_2O_2 whereas without TiO_2 present the lower concentrations of H_2O_2 are much less efficient in these decompositions. The surface of TiO_2 must therefore play a decisive role in sustaining the oxidative action of H_2O_2. In TiO_2-free solution the H_2O_2 decomposes by disproportionation into oxygen and water. This competes with the H_2O_2 reaction with agent explaining the incomplete nature of simulant degradation at the lower H_2O_2 concentration. In the presence of TiO_2 the H_2O_2 is bound to the surface forming peroxo complexes which do not undergo such disproportionation. The important role of TiO_2 which emerges from these studies is that it stabilizes the peroxide while maintaining its high oxidation power.

Due to the successful results using iron complexes as catalysts in the decomposition of organophosphates, experimental endeavors were undertaken using ferric ion loaded bentonite clays. The advantages of employing these clays is that they provide a large surface for catalytic activity and can be washed and possibly re-used for numerous degradative cycles. Both DBP and nitrophenol were either partially or totally decomposed in hydrogen peroxide containing bentonite-iron oxide suspensions. Thermal degradations of DBP using temperatures of ~70°C lead to approximately 70% decomposition after a time period of 3 hrs. Thermal decompositions at inferior temperatures of ~60°C lead to a lower percentage of degradation, i.e. ~55%. Concomitant irradiation, at this temperature, enhances the percentage of mineralization only slightly.

The necessity of loading the bentonite clay particles with Fe(III) is apparent from Figs 6 and 7. These Figures show that at room temperature, even under irradiation, no decomposition of nitrophenol occurs and even the higher temperature thermally (65°C) induced (non-irradiated) degradation occurs much less efficiently, in presence of unloaded bentonite. Using Fe(III) oligomer loaded clays, simultaneous irradiation and heating lead to the best results, higher temperatures pushing forward the initial reaction rate relative to the room temperature studies. The dark reaction at 65°C proceeds relatively rapidly initially, but again the theoretical CO_2 limit is not reached. Only by heating and irradiating at the same time is the theoretical CO_2 evolution limit

attained (see Fig. 8). The initial reaction rates of experiments performed at 65°C under irradiation in presence of iron loaded bentonite clays are comparable with the rates of light assisted experiments in homogeneous $Fe(NO_3)_3$ solution at room temperatures, although the theoretical CO_2 evolution limit is not attained in the latter (Fig. 6). TOC analyses corroborate these results.

Degradation of 4-chlorophenol in presence of bentonite - Fe(III) oligomer clays lead to results similar to those in the mineralisation of 4-nitrophenol, simultaneous heating and irradiation giving a more complete decomposition. Clays dried at 130°C were apparently more efficient catalysts than those baked at 500°C (Fig. 9). Irradiation at room temperature does lead to mineralisation although these experiments are less efficient in decomposition than those done at 65°C. Blank experiments performed at 27°C (with irradiation) in presence of unloaded bentonite clays lead to essentially no degradation (Fig. 10).

Preliminary experiments done previously using $Cu(SO_4)$ as a homogeneous catalyst proved the effectiveness of this complex as an activator in decomposing organophosphorous compounds. We consequently loaded bentonite clays with Cu(II) in order to test its feasibility as a catalyst in toxic compound degradations. Its effect was remarkable in the oxidative decomposition of nitrophenol (Fig. 11). The initial degradative reaction rates and most especially the final reaction rates increased greatly compared to those in presence of bentonite-iron clays. Room temperature (with simultaneous irradiation) studies again lead to incomplete decomposition.

EXPERIMENTAL PROCEDURES

All aqueous dispersions of the model compounds were prepared by injecting the appropriate quantity of 10^{-1}M simulant solution (THF solvent) onto the reaction vessels' walls and letting the solvent evaporate in the air until no traces of solvent are left, and subsequently redissolving the simulants in water. The TiO_2 powder (P25, Degussa 10 g/l) and/or catalytic agent are then added to the appropriate experiments, the solutions being stirred continuously.

The Fe(III) oligomer loaded bentonite clays were prepared according to the following procedure. One hundred grams of bentonite (Fluka) were suspended in 3 l distilled water under continuous stirring for 2 hours. The solution was then left to decant for 64 hours. The solid settled out and after was resuspended in water and left standing for approximately 3 hours. The bentonite particles remained only partially in suspension. This suspension was then centrifuged at 4000 rpm for 20 mins, and the precipitated solid resuspended in 500 ml of 1 M sodium acetate buffer (at pH 3.5, adjusted with acetic acid) and left to stand for approximately 16 hr in order to remove

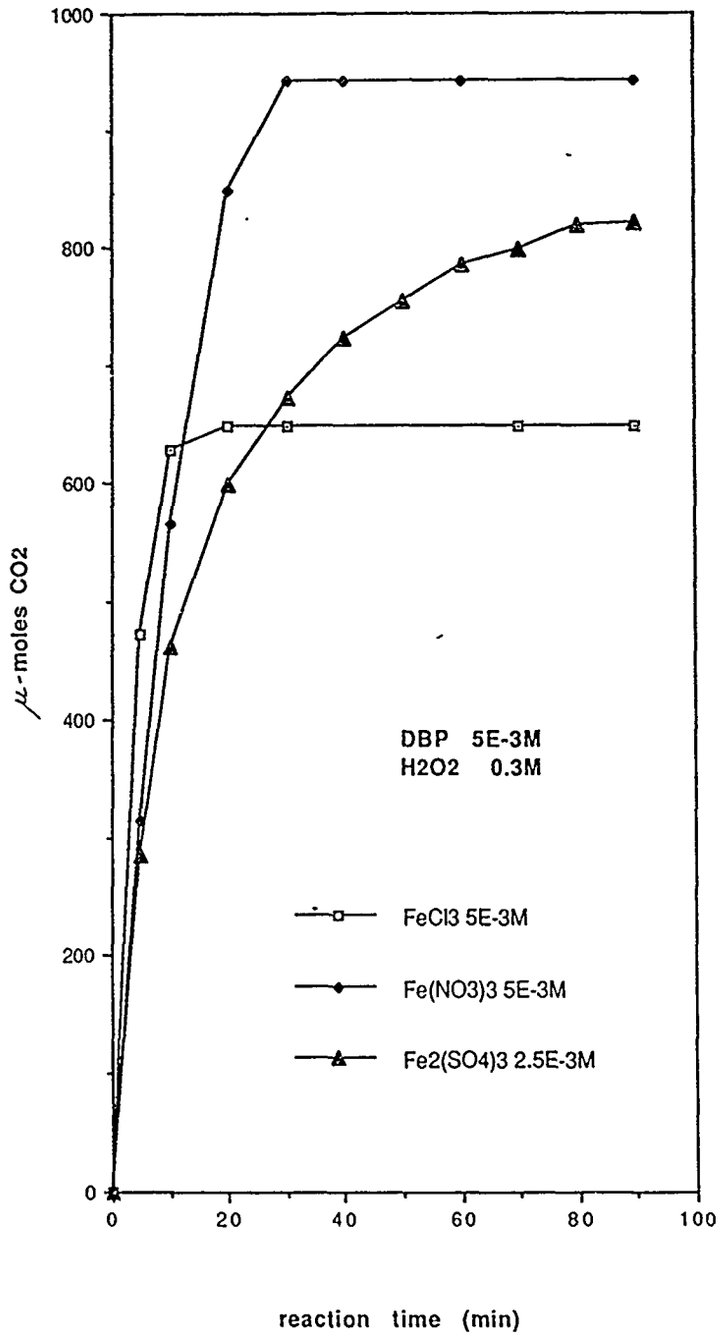
carbonates. The clay is then washed with water and centrifuged several times. This washed clay is suspended in 500 ml of 1M NaCl solution and then centrifuged and resuspended a second time in 500 ml of 1M NaCl. The clay is then washed with water and centrifuged repeatedly until complete removal of chloride (tested by $AgNO_3$) is assured.

The copper oxide loaded pillared bentonite clays were prepared according to the following procedure. Ten grams of purified bentonite (sodium salt intercalated) were suspended in ~700 ml water and stirred for 1 hour, after which 20 ml of a 1 M aqueous solution of $CuCl_2$ were added slowly under continual stirring for more than 1 hour. At this stage of the reaction the supernatant was light blue in color and the pH = 3.2. In order to form copper oxides a solution of 0.2 M NaOH was added dropwise over approximately 5 hours until the pH attained 6.25.

This solution was then left overnight. The following day the pH was remeasured and was found to remain the same, i.e. pH = 6.3. The supernatant, very light blue in color, was discarded and 600 ml of 10^{-2}M HCl were added in order to eliminate any excess of copper not intercalated. After this addition the pH fell to 4.5. More HCl was added until the pH dropped to 3.7. The mixture was then stirred for several minutes, centrifuged and rewashed with water many times. The color of the precipitate changed from light blue to yellow white. The addition of HCl was repeated once again as the color of the precipitate was not homogeneous. This precipitate was washed and centrifuged repeatedly until all chloride ions were eliminated. (These clays were poor in copper. It may be possible to obtain a product richer in copper if the neutralization with NaOH is performed after 24 hours.) The resulting loaded pillared clays were dried at 130°C for 1 hour and then at 500°C for 5 hours.

All experiments performed under artificial sunlight were done in a Hanau AM I solar simulator. The TOC (Total Organic Carbon) analyses were performed with a Shimadzu Total Organic Carbon Analyzer TOC-500.

FIGURE 1



Anion effect on DBP degradation

FIGURE 2

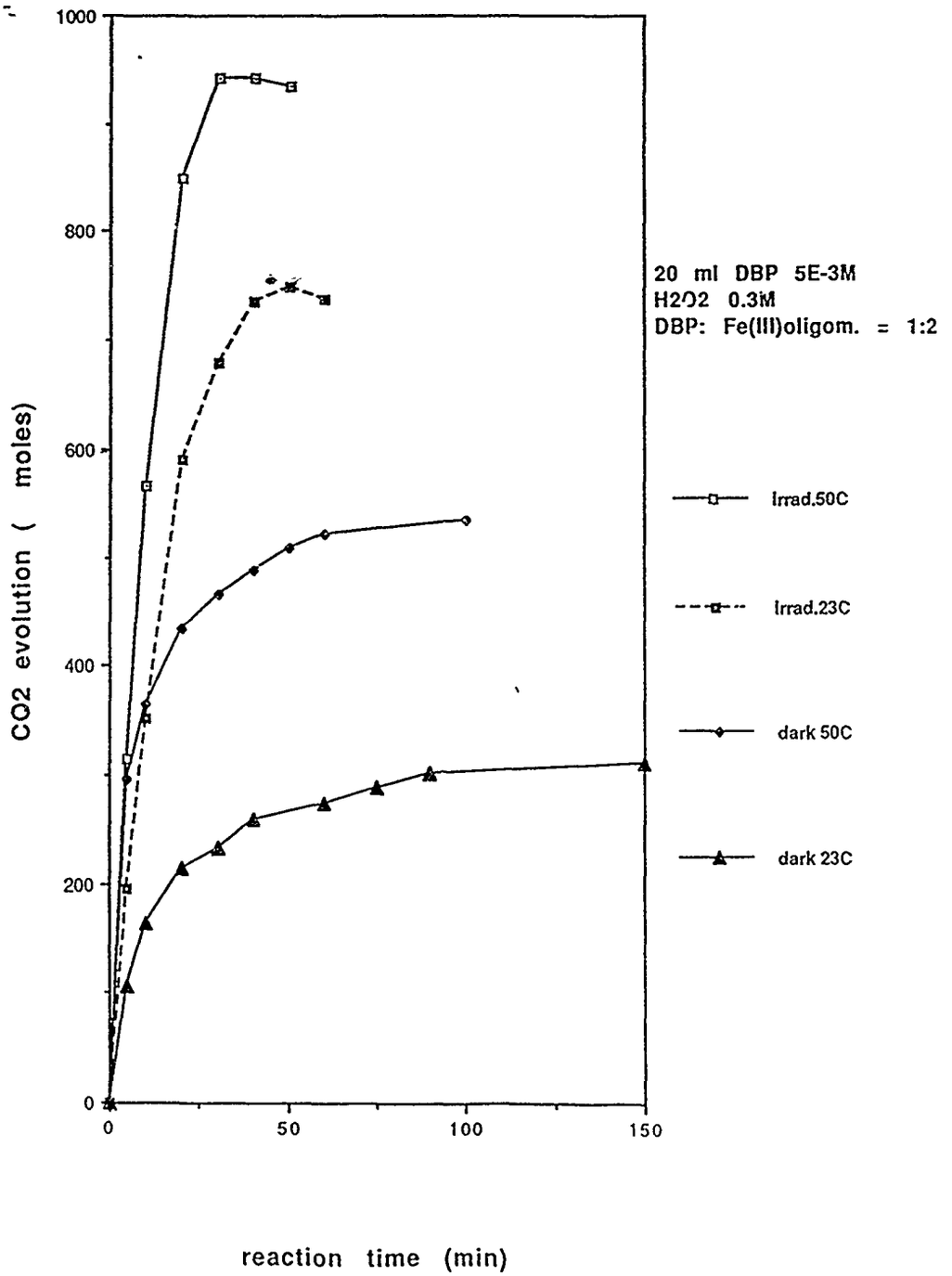
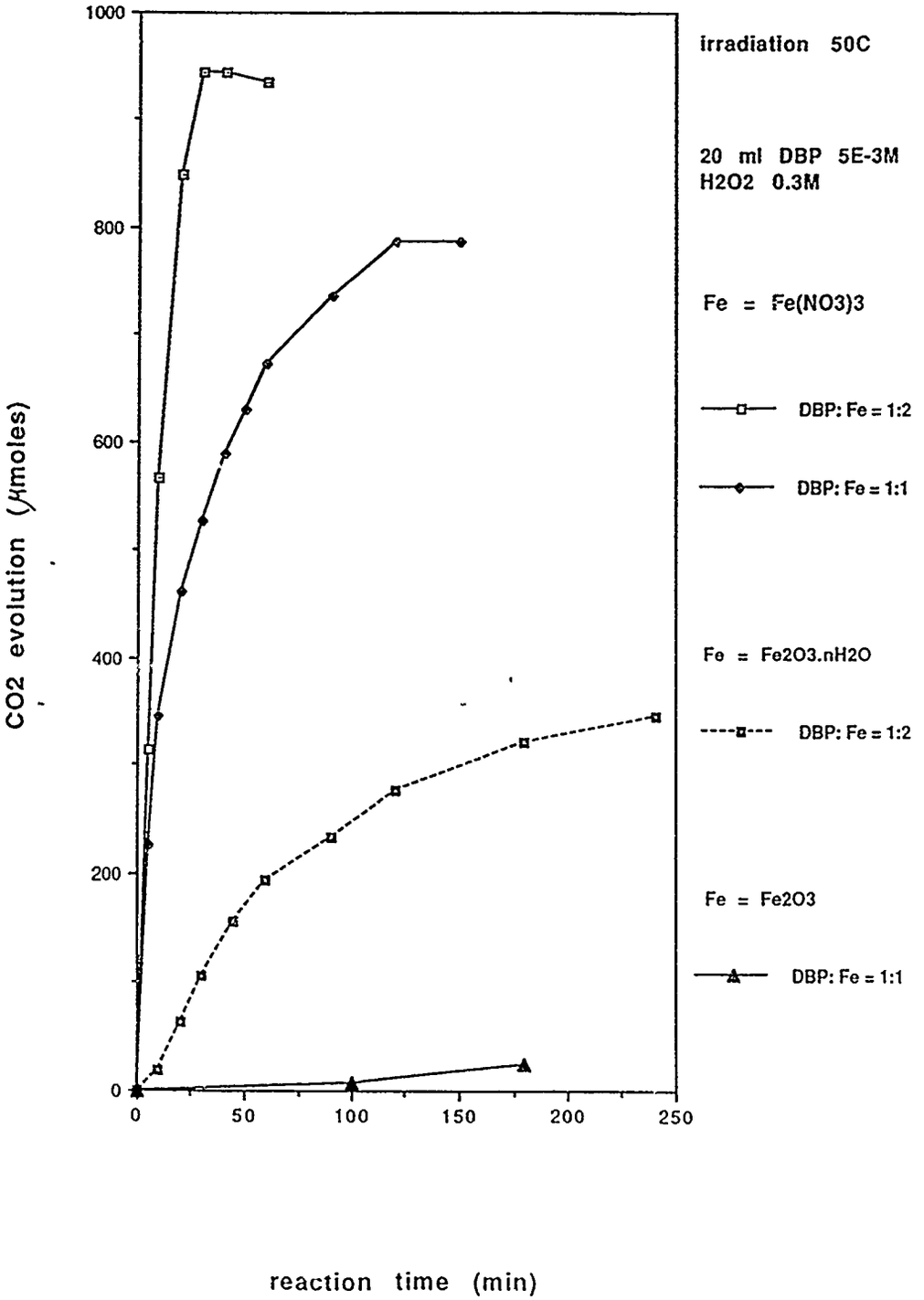
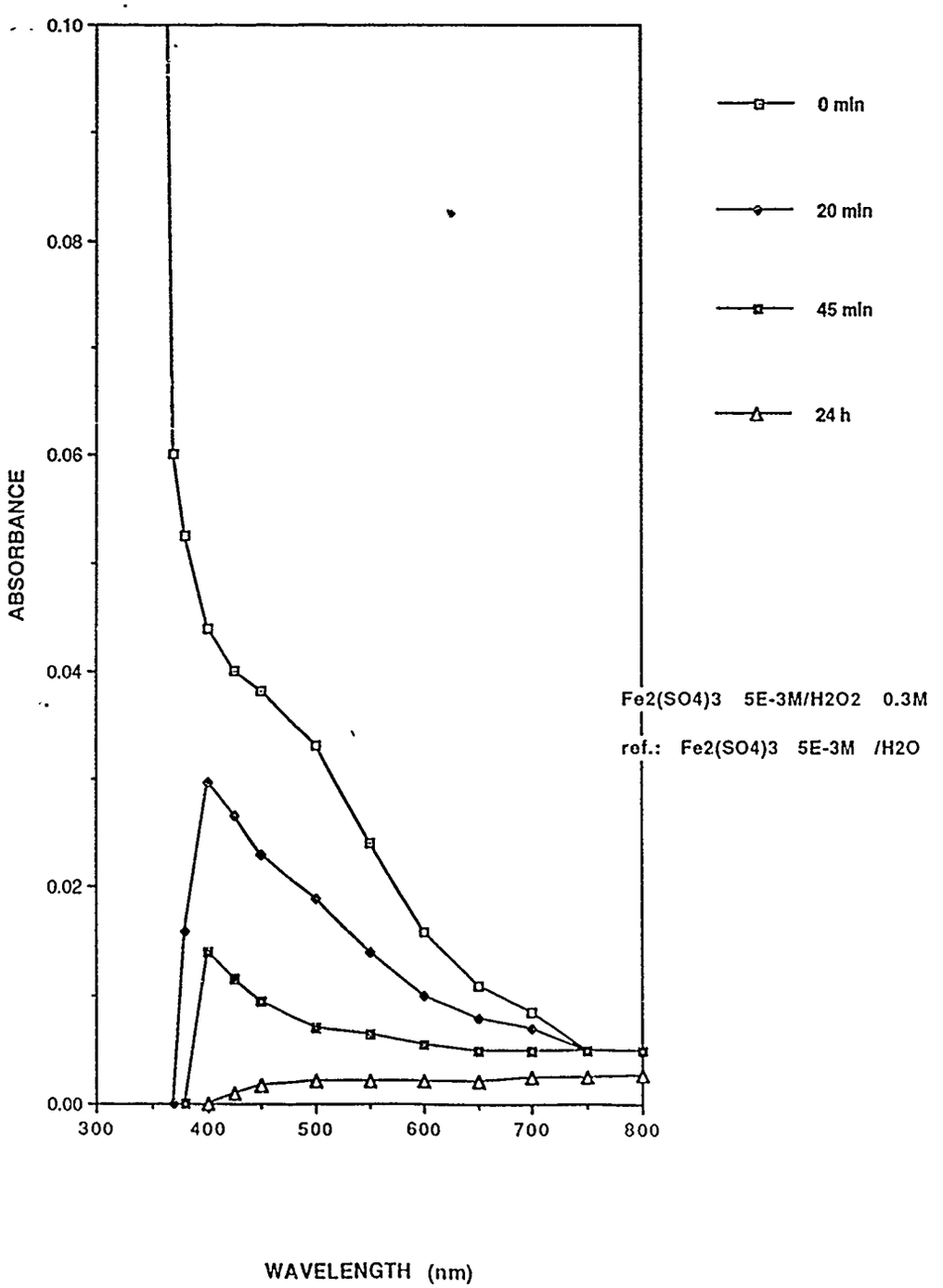

1000
800
600
400
200
0
0
50
100
150
CO2 evolution (moles)
reaction time (min)
20 ml DBP 5E-3M
H2O2 0.3M
DBP: Fe(III)oligom. = 1:2
Irrad.50C
Irrad.23C
dark 50C
dark 23C

FIGURE 3


1000
800
600
400
200
0
0
50
100
150
200
250
CO2 evolution (μmoles)
reaction time (min)
irradiation 50C
20 ml DBP 5E-3M
H2O2 0.3M
Fe = Fe(NO3)3
DBP: Fe = 1:2
DBP: Fe = 1:1
Fe = Fe2O3.nH2O
DBP: Fe = 1:2
Fe = Fe2O3
DBP: Fe = 1:1

FEGURE 4


0.10
0.08
0.06
0.04
0.02
0.00
ABSORBANCE
300
400
500
600
700
800
WAVELENGTH (nm)
0 min
20 min
45 min
24 h
Fe2(SO4)3 5E-3M/H2O2 0.3M
ref.: Fe2(SO4)3 5E-3M /H2O

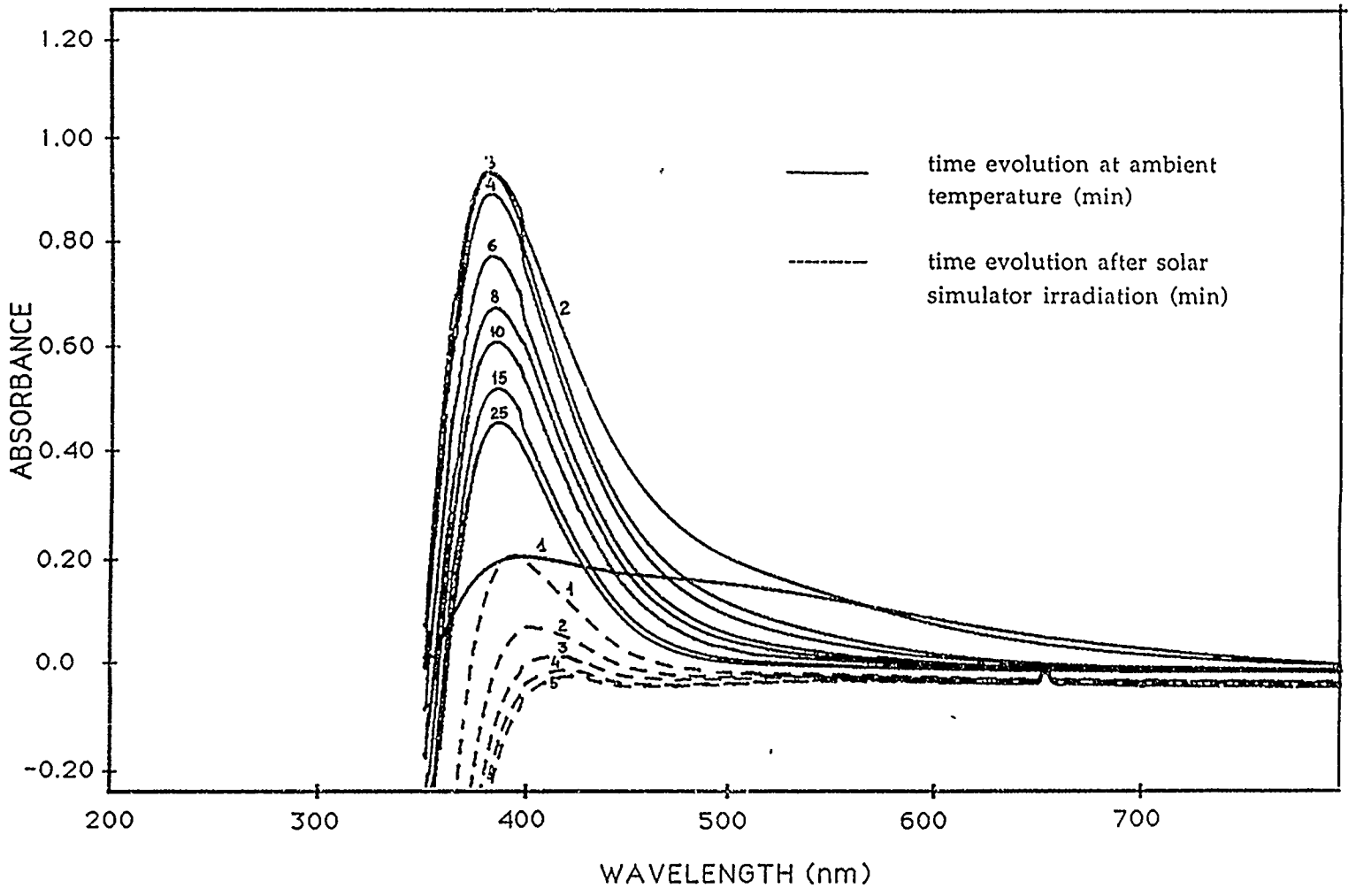

1.20
1.00
0.80
0.60
0.40
0.20
0.0
-0.20
ABSORBANCE
200
300
400
500
600
700
WAVELENGTH (nm)
time evolution at ambient temperature (min)
time evolution after solar simulator irradiation (min)
3
4
6
8
10
15
25
2
1
1
2
3
4
5

FIGURE 5

FIGURE 6

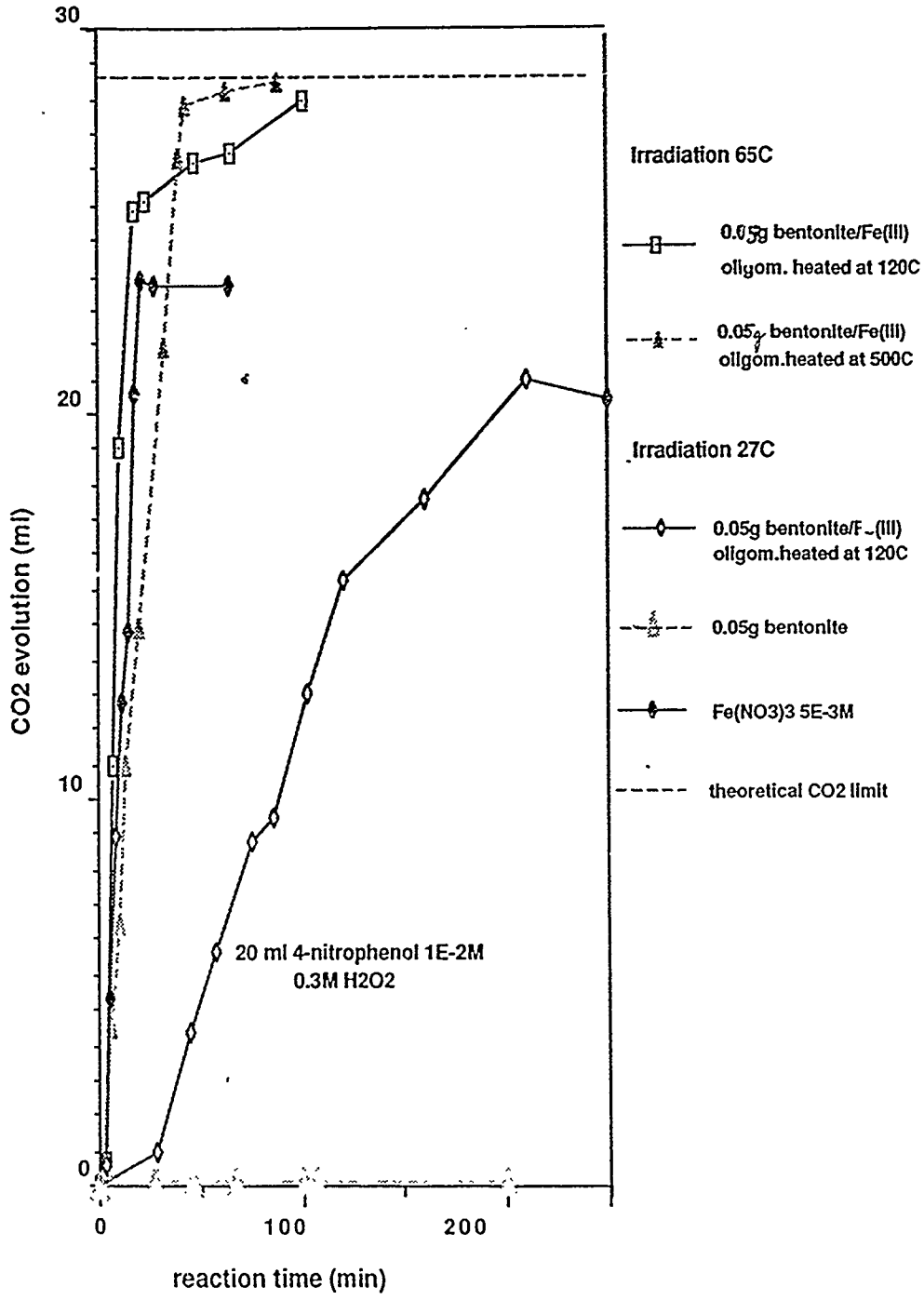

30
20
10
0
CO2 evolution (ml)
0
100
200
reaction time (min)
20 ml 4-nitrophenol 1E-2M
0.3M H2O2
Irradiation 65C
0.05g bentonite/Fe(III)
oligom. heated at 120C
0.05g bentonite/Fe(III)
oligom.heated at 500C
Irradiation 27C
0.05g bentonite/Fe(III)
oligom.heated at 120C
0.05g bentonite
Fe(NO3)3 5E-3M
theoretical CO2 limit

FIGURE 7

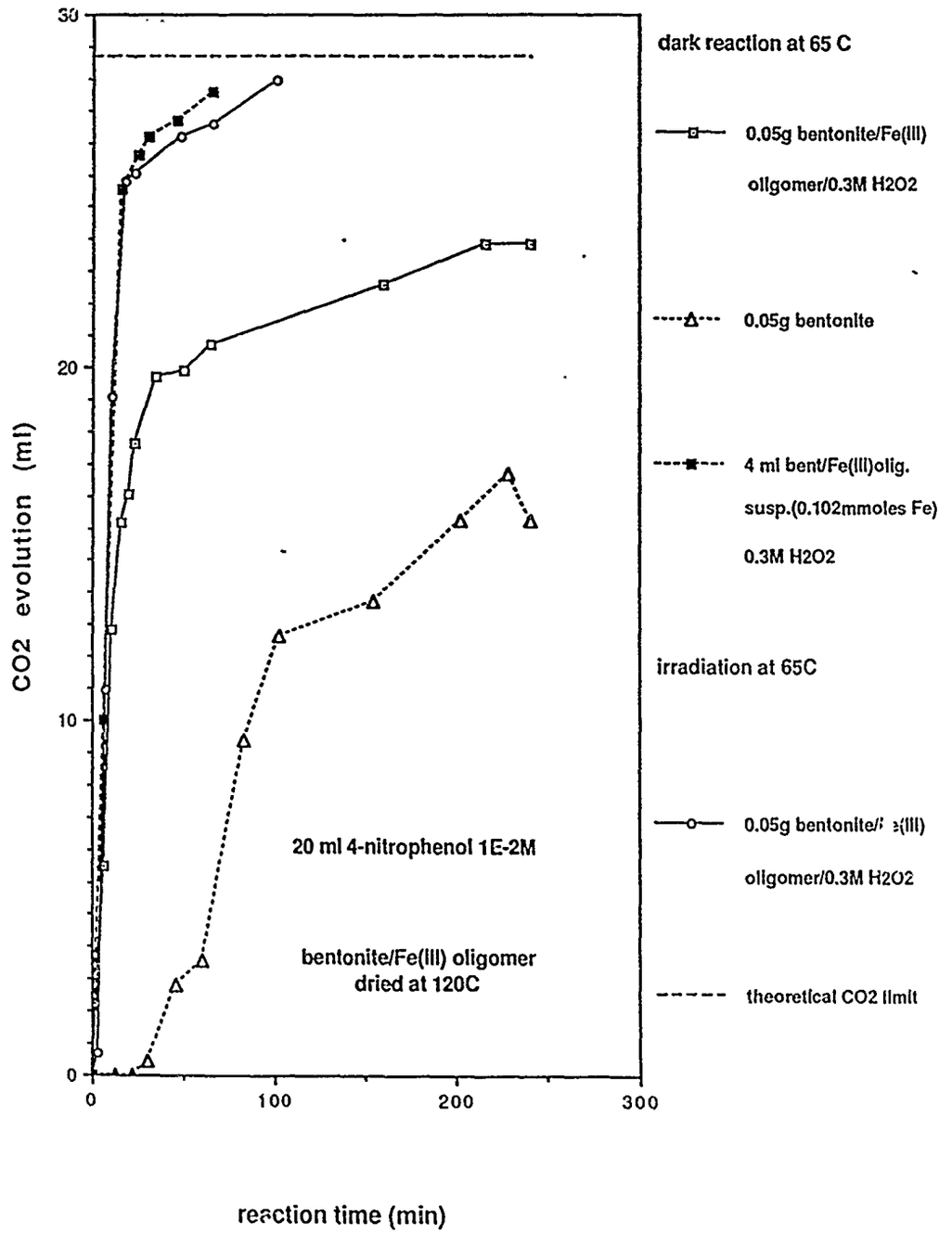

30
20
10
0
0
100
200
300
CO2 evolution (ml)
reaction time (min)
20 ml 4-nitrophenol 1E-2M
bentonite/Fe(III) oligomer
dried at 120C
dark reaction at 65 C
0.05g bentonite/Fe(III)
oligomer/0.3M H2O2
0.05g bentonite
4 ml bent/Fe(III)olig.
susp.(0.102mmoles Fe)
0.3M H2O2
irradiation at 65C
0.05g bentonite/Fe(III)
oligomer/0.3M H2O2
theoretical CO2 limit

FIGURE 8

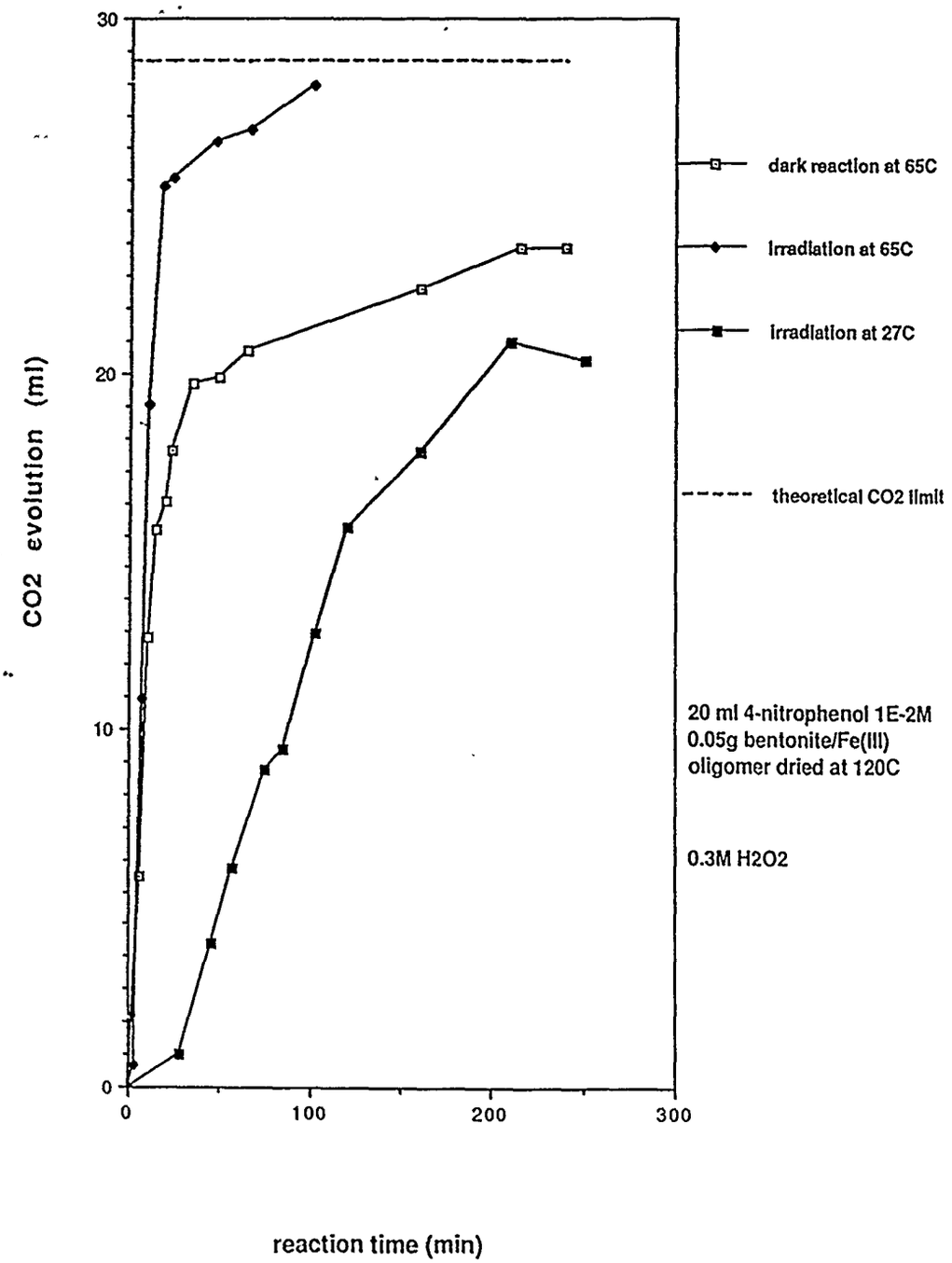

30
20
10
0
0
100
200
300
CO2 evolution (ml)
reaction time (min)
dark reaction at 65C
Irradiation at 65C
Irradiation at 27C
theoretical CO2 limit
20 ml 4-nitrophenol 1E-2M
0.05g bentonite/Fe(III)
oligomer dried at 120C
0.3M H2O2

FIGURE 9

4-Chlorophenol degradation

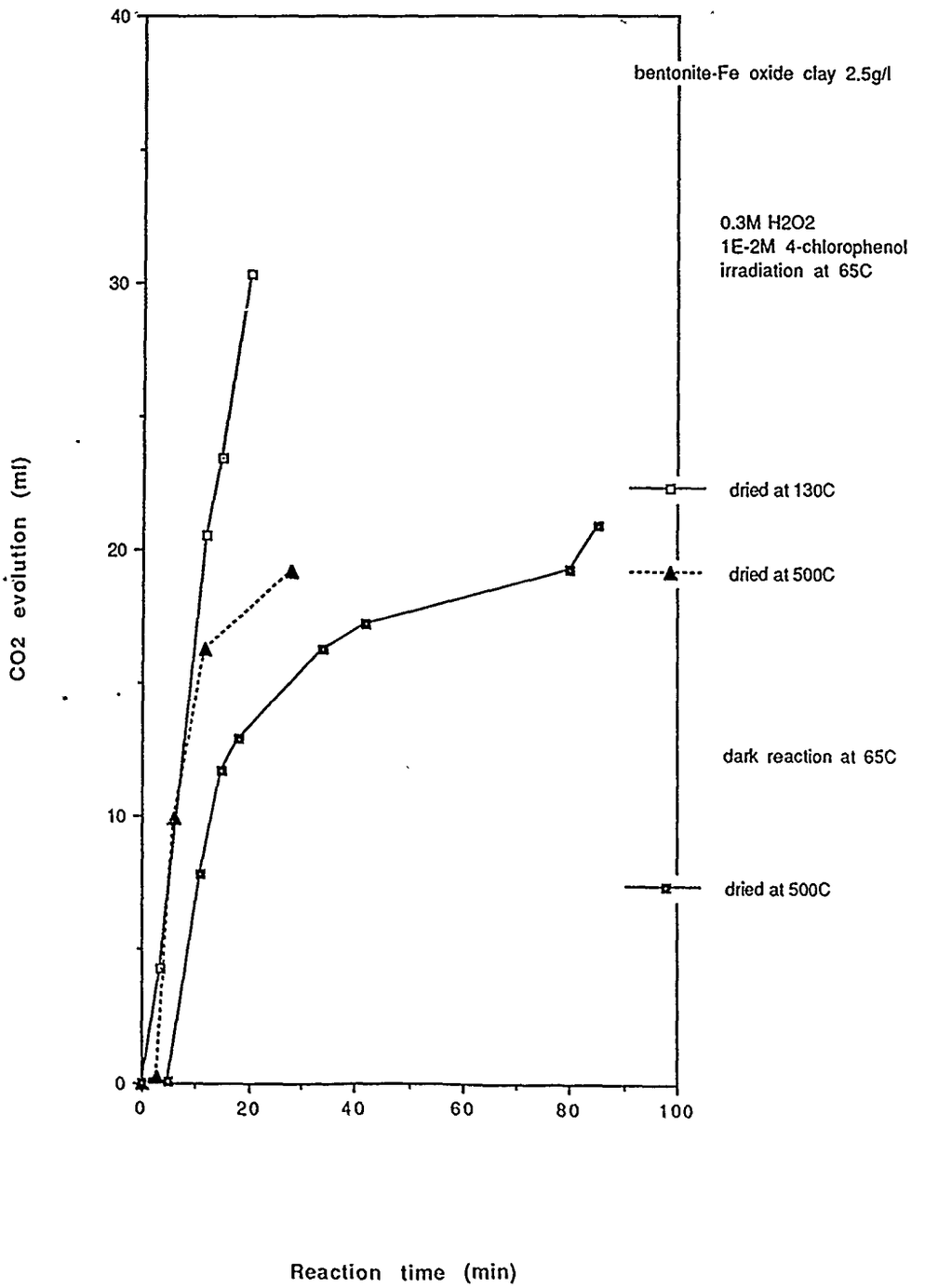


FIGURE 10

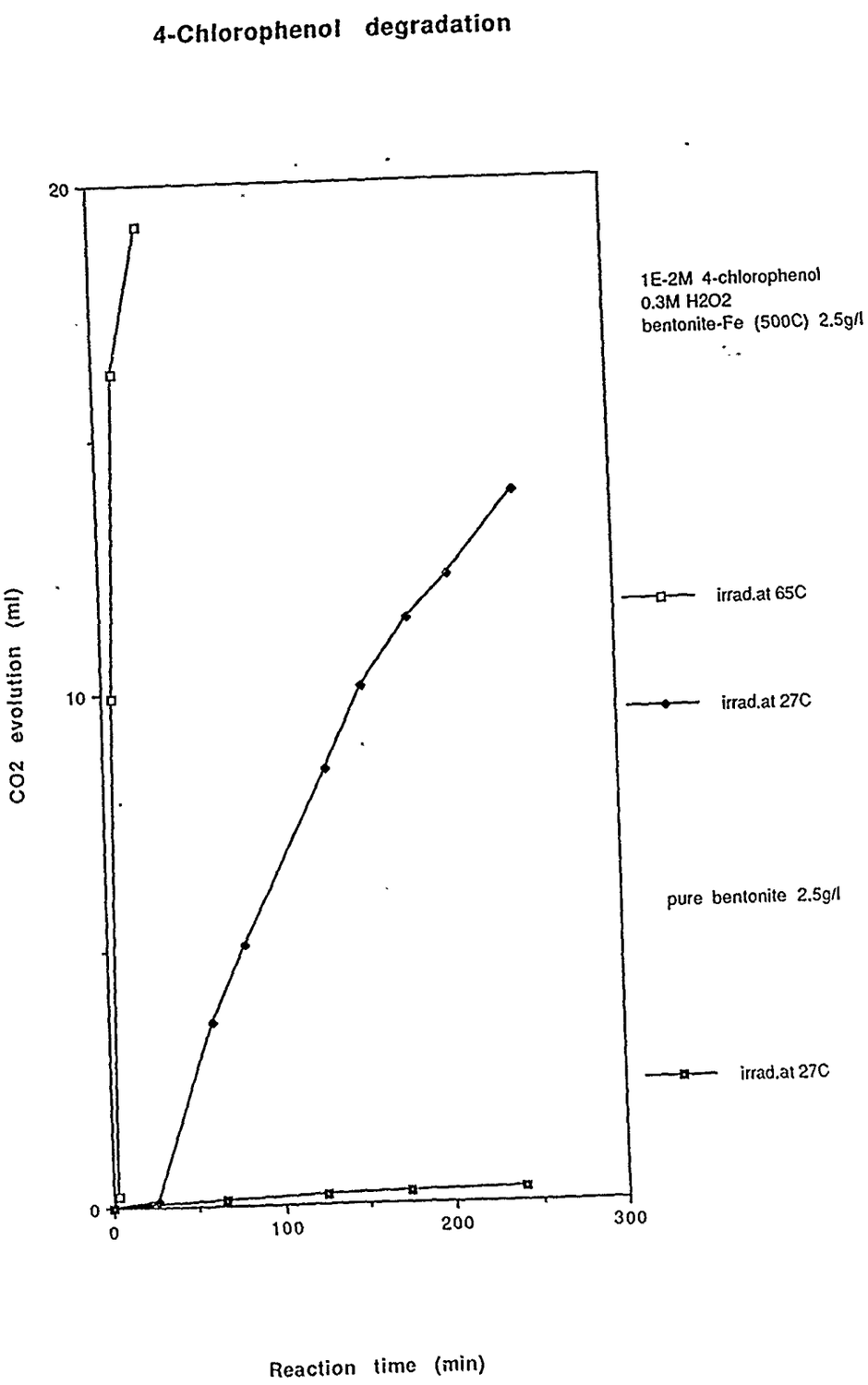
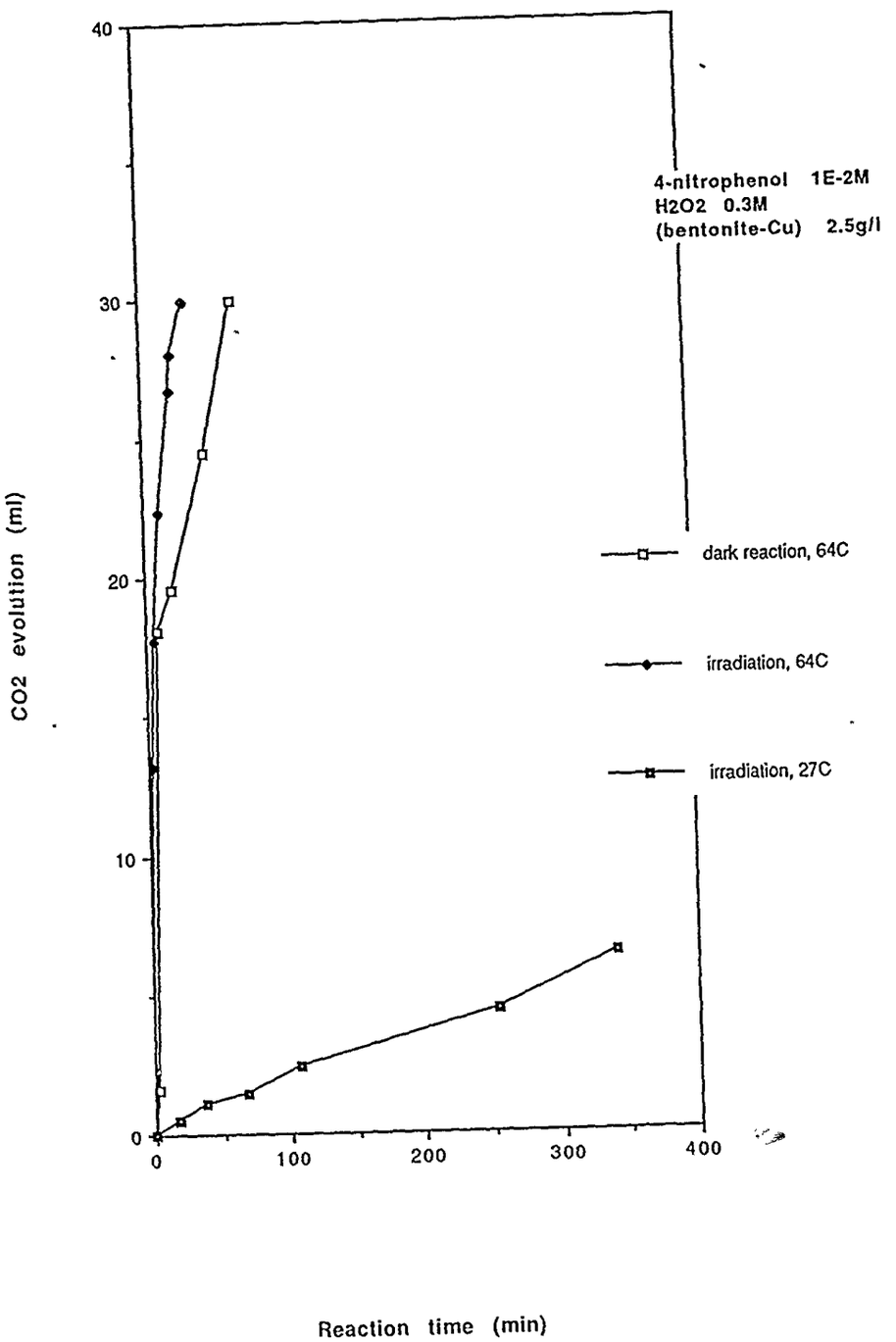

4-Chlorophenol degradation
20
10
0
0
100
200
300
CO2 evolution (ml)
Reaction time (min)
1E-2M 4-chlorophenol
0.3M H2O2
bentonite-Fe (500C) 2.5g/l
irrad.at 65C
irrad.at 27C
pure bentonite 2.5g/l
irrad.at 27C

FIGURE 11

4-Nitrophenol degradation in presence of bentonite-Cu oxide